



TITLE:

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Dithiocarbonates

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General, High Yield Synthesis of α -Oxoketene Dithioacetals and *O*-(1-Alkoxy-2,2-dialkyl)vinyl *N,N*-Diisopropylammonium Dithiocarbonates¹⁾

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Several α -alkoxycarbonyl ketene dithioacetals have been prepared in excellent yields (79–87%) by the reaction of lithium ester enolates with carbon disulfide followed by treatment with alkyl halides. One equivalent of LDA was required for the overall conversion while it has been previously reported that two equivalents of a base are needed to effect this transformation. A plausible mechanism, in the light of available literature, has been proposed. Moreover, *O*-(1-alkoxy-2,2-dialkyl)vinyl *N,N*-diisopropylammonium dithiocarbonates were obtained when lithium enolates derived from esters having only one α -hydrogen were reacted with carbon disulfide followed by treatment with chlorotrimethylsilane. No *S*-trimethylsilylated products were obtained.

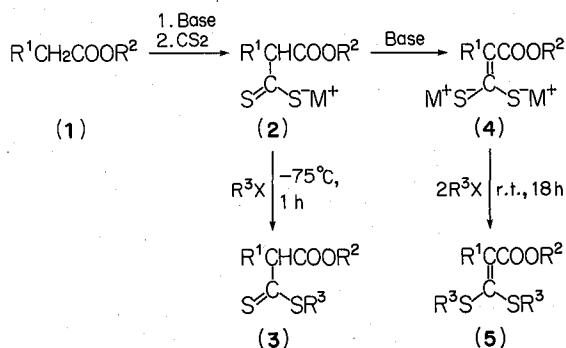
KEY WORDS: α -Alkoxycarbonyl Ketene Dithioacetal/ Carbon Disulfide/
Lithium Ester Enolate/ *O*-(1-Alkoxy-2,2-dialkyl)vinyl *N,N*-
Diisopropylammonium Dithiocarbonate/
Chlorotrimethylsilane/

The ketene dithioacetals having an α -keto group are versatile intermediates²⁾ which can be reacted under variety of conditions as substrates for sequential carbon-carbon bond forming reactions and also hold considerable potential for functional group manipulations. The versatility of these compounds has previously been demonstrated by their use in the synthesis of heterocycles^{3–6)}, Diels-Alder dienes⁷⁾ and in the indirect synthesis of tertiary alkylated ketones⁸⁾. Their reactions with Grignard and Reformatsky reagents leading to the construction of aromatic and heteroaromatic skeleta have recently been shown to be of general applicability⁹⁾. These studies are limited, however, to ketene dithioacetals derived from ketones while those derived from esters have been neglected, probably, because only few of these are known up to date^{10–12)}, to the best of our knowledge.

The ketones are easily transformed to α -oxoketene dithioacetals by the reaction with carbon disulfide in the presence of a base followed by alkylation. Several bases^{8,13,14)} can be employed but sodium hydride¹⁴⁾ is generally preferred. However, simple esters when treated with a sodium hydride-carbon disulfide-methyl iodide combination afforded products arising from the Claisen condensation¹⁴⁾. Dieter¹¹⁾ studied the use of various amide bases, such as lithium diisopropylamide (LDA), lithium dicyclohexylamide (LCA) and lithium hexamethyldisilazanide (LHMDS) in the presence of one equivalent of hexamethylphosphoric triamide (HMPA) for the genera-

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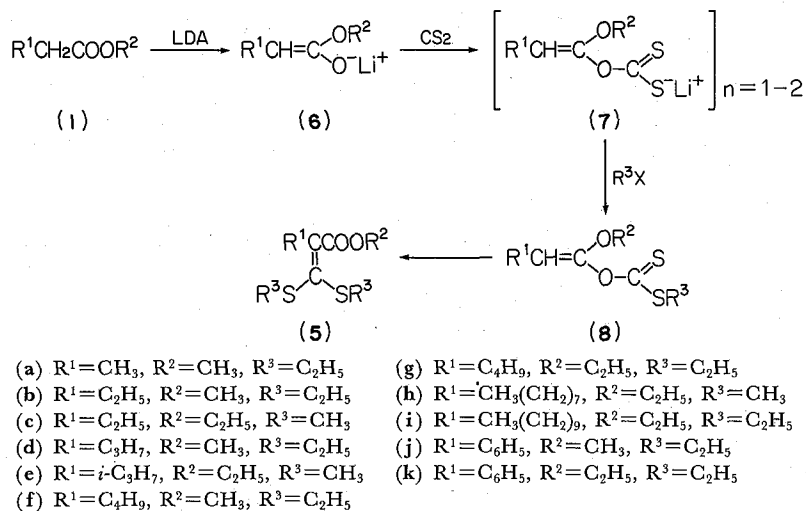
tion of lithium enolates from active methylene compounds followed by treatment with carbon disulfide and alkyl halide in an effort to develop a more general strategy to α -oxoketene dithioacetals. While ketones were converted to α -oxoketene dithioacetals in high yields by the use of all these bases, good yields from a lactone and an α,β -unsaturated ester were obtained only by the use of LHMDS; low yields of the desired products and significant amount of condensation products were obtained when LDA was employed as the base. No example of conversion of simple ester to the corresponding ketene dithioacetal is described. Konen and his co-workers¹⁰ studied the reaction of α -anion of carboxylate salts and esters with carbon disulfide followed by alkylation. Two examples of conversion of lithium ester enolates, generated by the use of lithium isopropyl cyclohexylamide, to α -alkoxycarbonyl ketene dithioacetals have been described; the product was isolated and characterized in one case while the product formation was detected by gas chromatography and NMR analysis in the other case. Scheme 1 shows the general course of the reaction. It is important to mention here that while the alkylation of **2** was complete in 1 hour at -75°C , the alkylation of **4** took 18 hours at room temperature which leaves some doubt on the mechanism of the reaction.



Scheme 1.

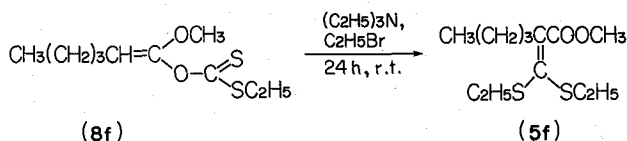
We wish to report here the first synthesis of ketene dithioacetals (**5**) having an α -alkoxycarbonyl group from esters **1** by an overall use of one equivalent of LDA as the base. The results will help in the better understanding of the reaction of enolates (**6**) with carbon disulfide. It has been reported that the use of LDA as the base results in the formation of large amount of condensation products and low yields of the ketene dithioacetals¹¹. Thus, the reaction of lithium enolate **6a**, generated with LDA from methyl propionate (**1a**)¹⁵, with carbon disulfide at -78°C followed by treatment with ethyl bromide furnished, after aqueous workup and distillation, pure α -methoxycarbonyl ketene dithioacetal **5a** in 87% yield. Various α -alkoxycarbonyl ketene dithioacetal derivatives **5b-k** were synthesized accordingly (Table I). The spectral and analytical data of the products was in good agreement with the assigned structure (Table III). No condensation products were obtained in any case and the ^1H -NMR spectra of the crude products showed only the presence of the desired products. Although one equivalent of carbon disulfide and two equivalents of alkyl halide were sufficient, better yields were obtained when these were used in three equivalents which may be accounted

to the presence of diisopropylamine which is coproduced¹⁶⁾.



Scheme 2.

The reaction was usually complete when the reaction mixture, after the addition of alkyl halide, was left stirring overnight at room temperature. In some cases, however, the crude product was analyzed to be a mixture of **5** and **8** by the ¹H-NMR spectral data (Entry 5, 7 and 13 in Table I). An extension of the reaction time to two days, in these cases, did not show any trace of **8** suggesting that **8** is an intermediate which is slowly converted to **5** under the reaction conditions. This was supported by the fact that when we treated, in a separate experiment, the mixture of **5f** and **8f** obtained in Entry 7 (Table I), with triethylamine and ethyl bromide at room temperature for one day, the usual workup of the reaction mixture afforded pure **5f**.



We then attempted the synthesis of *O*-(1-alkoxy-2,2-dialkyl)vinyl *S*-trimethylsilyl dithiocarbonate derivatives (**10**) from esters with only one α -hydrogen. Thus, lithium enolate, generated from ethyl isobutyrate (**9b**), was reacted with carbon disulfide at -78°C followed by treatment with chlorotrimethylsilane (CTMS) for 30 min. Removal of the precipitated lithium bromide by filtration and evaporation of the solvent furnished a viscous red liquid. Treatment of this liquid with ether-dichloromethane resulted in the crystallization of a red solid which was characterized as *O*-(1-ethoxy-2,2-dimethyl)vinyl *N,N*-diisopropylammonium dithiocarbonate (**11b**) on the basis of analytical and spectral data (Table III). No *S*-trimethylsilylated product (**10**) was formed. Several *O*-(1-alkoxy-2,2-dialkyl)vinyl *N,N*-diisopropylammonium dithiocarbonates

Table I. Preparation of 5

Entry	Substrate	Alkyl halide	Reaction time (day)	Product	Yield ^{a)} (%)	Bp (°C/mmHg)	Molecular formula
1	1a	C ₂ H ₅ Br	1	5a	87	104–108/3	C ₉ H ₁₆ O ₂ S ₂ (220.4)
2	1b	C ₂ H ₅ Br	1	5b	85	100–103/2.5	C ₁₀ H ₁₈ O ₂ S ₂ (234.4)
3	1c	CH ₃ I	1	5c	82	107–112/3	C ₉ H ₁₆ O ₂ S ₂ (220.4)
4	1d	C ₂ H ₅ Br	1	5d	83	102–106/3	C ₁₁ H ₂₀ O ₂ S ₂ (248.4)
5	1e	CH ₃ I	1	5e	65 ^{b)}	108–112/4	C ₁₀ H ₁₈ O ₂ S ₂ (234.4)
6	1e	CH ₃ I	2	5e	81		
7	1f	C ₂ H ₅ Br	1	5f	50 ^{c)}	107–110/2.5	C ₁₂ H ₂₂ O ₂ S ₂ (262.4)
8	1f	C ₂ H ₅ Br	2	5f	79		
9	1g	C ₂ H ₅ Br	1	5g	80	122–127/3	C ₁₃ H ₂₄ O ₂ S ₂ (276.5)
10	1h	CH ₃ I	1	5h	84	153–157/3	C ₁₅ H ₂₈ O ₂ S ₂ (304.5)
11	1i	C ₂ H ₅ Br	1	5i	85	158–162/0.5	C ₁₉ H ₃₆ O ₂ S ₂ (360.6)
12	1j	C ₂ H ₅ Br	1	5j	79	Decomposed	C ₁₄ H ₁₈ O ₂ S ₂ (282.4)
13	1k	C ₂ H ₅ Br	1	5k	30 ^{d)}	Decomposed	C ₁₅ H ₂₀ O ₂ S ₂ (296.4)
14	1k	C ₂ H ₅ Br	2	5k	80		

^{a)} Isolated yield by distillation, if otherwise noted.

^{b)} Determined by ¹H-NMR data of the obtained product before distillation. Contained 35% of 8e: δ , J (Hz) (CDCl₃/TMS) 1.01 (d, 6H, J=7.0), 1.22 (t, 3H, J=7.2), 2.63 (s, 3H), 2.64 (m, 1H), 3.89 (d, 1H, J=10.4), 4.15 (m, 2H).

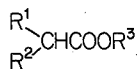
^{c)} Determined by ¹H-NMR as above. Contained 50% of 8f: δ , J (Hz) (CDCl₃/TMS) 0.89 (m, 3H), 1.21 (m, 3H), 1.32 (m, 4H), 2.03 (m, 2H), 3.22 (q, 2H, J=7.4), 3.69 (s, 3H), 4.10 (t, 1H, J=7.0).

^{d)} Determined by ¹H-NMR as above. Contained 70% of 8k: δ , J (Hz) (CDCl₃/TMS) 1.26 (m, 6H), 3.17 (q, 2H, J=7.0), 4.11 (q, 2H, J=7.2), 5.33 (s, 1H), 7.36 (m, 3H), 7.51 (m, 2H).

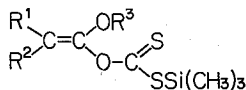
(11) prepared accordingly are given in Table II. These products are stable when in the solid state but decompose slowly in solution to 12. The compound 12 was obtained in significant amount in all the cases. The products 11f and 11g could not be isolated while the ¹H-NMR spectra of the crude product showed the presence of only desired product. The compounds 11 were not obtained when CTMS was not added.

The formation of α -alkoxycarbonyl ketene dithioacetals (5) can be explained through the intermediacy of 8. Though the transformation of esters 1 to 8¹⁷⁾ can simply be explained by the attack of oxygen of ester enolate 6 on the carbon disulfide followed by alkylation, a mechanism involving lithium enolate aggregates seems more probable since it is now believed that lithium enolates exist as aggregates.^{18,19)} The exact nature of the lithium ester enolates 6, i.e. dimeric, tetrameric or hexameric, is not known but the formation of 8 can best be explained, in the light of available literature, assuming a dimeric structure of the enolate²⁰⁾ analogous to the mechanism proposed for the formation of ate complex¹⁹⁾ by the addition of HMPA to a lithium enolate. The plausible mechanism is outlined in Scheme 3. The enolate unit in 13 can attain charge density through complexation of the Li with S of CS₂ (see 14), the enolate oxygen atom being still neutralized by two Li⁺. Through reorganization, the S may become part of the aggregate nucleus 15, the enolate oxygen outside being neutralized only by one Li⁺, which should increase the nucleophilicity. An interaction between O of enolate and C of carbon disulfide can give 7 which will furnish 8 on alkylation. The actual mechanism

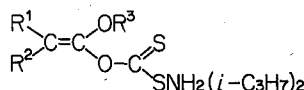
Reaction of Lithium Enolates with Carbon Disulfide



(9)

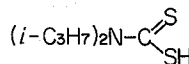


(10)



(11)

- (a) $\text{R}^1=\text{CH}_3$, $\text{R}^2=\text{CH}_3$, $\text{R}^3=\text{CH}_3$
 (b) $\text{R}^1=\text{CH}_3$, $\text{R}^2=\text{CH}_3$, $\text{R}^3=\text{C}_2\text{H}_5$
 (c) $\text{R}^1=\text{CH}_3$, $\text{R}^2=\text{CH}_3$, $\text{R}^3=i\text{-C}_3\text{H}_7$
 (d) R^1 and $\text{R}^2=-(\text{CH}_2)_5-$, $\text{R}^3=\text{CH}_3$
 (e) R^1 and $\text{R}^2=-(\text{CH}_2)_5-$, $\text{R}^3=i\text{-C}_3\text{H}_7$
 (f) $\text{R}^1=\text{C}_2\text{H}_5$, $\text{R}^2=\text{C}_2\text{H}_5$, $\text{R}^3=\text{C}_2\text{H}_5$
 (g) R^1 and $\text{R}^2=-(\text{CH}_2)_4-$, $\text{R}^3=\text{CH}_3$



(12)

for the conversion of **8** to **5** is not clear but it can be said firmly that it does not follow the mechanism outlined in Scheme 1 because in that case one more equivalent of LDA would have been required.¹⁷⁾

The mechanism for the conversion of esters **9** to *O*-(1-alkoxy-2,2-dialkyl)vinyl *N,N*-diisopropylammonium dithiocarbonates (**11**) is not clearly understood. It is not clear why *O*-(1-alkoxy-2,2-dialkyl)vinyl *S*-trimethylsilyl dithiocarbonates (**10**) were not obtained when CTMS was added to a solution containing *O*-(1-alkoxy-2,2-dialkyl)vinyl dithiocarbonate anion, derived from esters having one α -hydrogen and what is the role of CTMS in the formation of **11** which are not obtained when CTMS is not added.

In conclusion, the synthesis of α -alkoxycarbonyl ketene dithioacetals (**5**) has been achieved in excellent yields from carboxylic esters **1** by the reaction of their lithium enolates, generated by the use of LDA, with carbon disulfide followed by treatment with alkyl halides. This represents the first example of the transformation of **1** to **5** by an overall use of one equivalent of base and will be helpful in the better understanding of the reaction of enolates with carbon disulfide. The *O*-(1-alkoxy-2,2-dialkyl)vinyl *N,N*-diisopropylammonium dithiocarbonates (**11**) were obtained when lithium *O*-(1-alkoxy-2,2-dialkyl)vinyl dithiocarbonates were treated with CTMS.

Table II. Preparation of 11

Entry	Substrate	Product	Yield ^{a)} (%)	Mp (°C)	Molecular formula
1	9a	11a	27	85–86	C ₁₂ H ₂₅ NO ₂ S ₂ (279.5)
2	9b	11b	37	100	C ₁₃ H ₂₇ NO ₂ S ₂ (293.5)
3	9c	11c	30	86–87	C ₁₄ H ₂₉ NO ₂ S ₂ (307.5)
4	9d	11d	35	112	C ₁₅ H ₂₉ NO ₂ S ₂ (319.5)
5	9e	11e	37	96–97	C ₁₇ H ₃₃ NO ₂ S ₂ (347.6)
6	9f	11f	— ^{b)}		
7	9g	11g	— ^{b)}		

^{a)} Isolated yield by recrystallization.

^{b)} ¹H-NMR spectrum of the crude product showed only the presence of desired product but could not be isolated by recrystallization and decomposed to give **12** and condensation product.

Table III. Spectral Data of **5** and **11**

Product ^{a)}	IR $\nu_{\max}(\text{cm}^{-1})^b)$	¹ H-NMR (CDCl ₃ /TMS) δ , J (Hz)	MS m/z (%) ^{c)}
5a	1726	1.22 (m, 6H), 2.16 (s, 3H), 2.78 (m, 4H), 3.77 (s, 3H)	220 (45)
5b	1727	1.01 (t, 3H, J=7.4), 1.18 (m, 6H), 2.60 (q, 2H, J=7.4), 2.75 (m, 4H), 3.75 (s, 3H)	234 (31)
5c	1720	1.02 (t, 3H, J=7.4), 1.30 (t, 3H, J=7.2), 2.26 (s, 3H), 2.29 (s, 3H), 2.58 (q, 2H, J=7.4), 4.23 (q, 2H, J=7.2)	220 (55)
5d	1725	0.88 (t, 3H, J=7.2), 1.18 (m, 6H), 1.29 (m, 2H), 2.55 (t, 2H, J=7.2), 2.72 (m, 4H), 3.73 (s, 3H)	248 (47)
5e	1720	1.07 (d, 6H, J=7.0), 1.32 (t, 3H, J=7.0), 2.23 (s, 3H), 2.30 (s, 3H), 3.28 (m, 1H), 4.25 (q, 2H, J=7.2)	234 (30)
5f	1726	0.88 (t, 3H, J=7.0), 1.21 (m, 6H), 1.34 (m, 4H), 2.59 (t, 2H, J=7.6), 2.74 (m, 4H), 3.76 (s, 3H)	262 (39)
5g	1721	0.88 (t, 3H, J=7.2), 1.30 (m, 13H), 2.60 (t, 2H, J=7.2), 2.74 (m, 4H), 4.23 (q, 2H, J=7.2)	276 (29)
5h	1720	0.83 (t, 3H, J=6.6), 1.25 (m, 15H), 2.24 (s, 3H), 2.27 (s, 3H), 2.53 (t, 2H, J=7.0), 4.20 (q, 2H, J=7.2)	304 (28)
5i	1724	0.84 (t, 3H, J=6.8), 1.25 (m, 25H), 2.57 (t, 2H, J=8.0), 2.73 (m, 4H), 4.21 (q, 2H, J=7.2)	360 (21)
5j	1723	1.16 (t, 3H, J=7.2), 1.30 (t, 3H, J=7.2), 2.67 (q, 2H, J=7.2), 2.86 (q, 2H, J=7.2), 3.75 (s, 3H), 7.34 (s, 5H)	282 (35)
5k	1720	1.29 (m, 9H), 2.69 (q, 2H, J=7.4), 2.86 (q, 2H, J=7.4), 4.21 (q, 2H, J=7.0), 7.36 (s, 5H)	296 (27)
11a	1720	1.47 (d, 12H, J=6.6), 1.62 (s, 6H), 3.49 (m, 2H), 3.67 (s, 3H), 8.40 (bs, 2H)	178 (35)
11b	1718	1.20 (t, 3H, J=7.0), 1.44 (d, 12H, J=6.6), 1.59 (s, 6H), 3.49 (m, 2H), 4.11 (q, 2H, J=7.0), 7.30 (bs, 2H)	192 (38)
11c	1704	1.18 (d, 6H, J=6.2), 1.46 (d, 12H, J=6.6), 1.59 (s, 6H), 3.46 (m, 2H), 5.01 (m, 1H), 8.45 (bs, 2H)	206 (15)
11d	1708	1.45 (d, 12H, J=6.8), 1.50 (m, 6H), 2.03 (dt, 2H, J ₁ =1.8, J ₂ =14.5), 2.40 (d, 2H, J=14.5), 3.51 (m, 2H), 3.69 (s, 3H), 7.75 (bs, 2H)	218 (30)
11e	1717	1.20 (d, 6H, J=6.2), 1.45 (d, 12H, J=6.8), 1.50 (m, 6H), 2.20 (dt, 2H, J ₁ =1.6, J ₂ =13.2), 2.62 (d, 2H, J=13.2), 3.48 (m, 2H), 5.07 (m, 1H), 7.30 (bs, 2H)	246 (22)

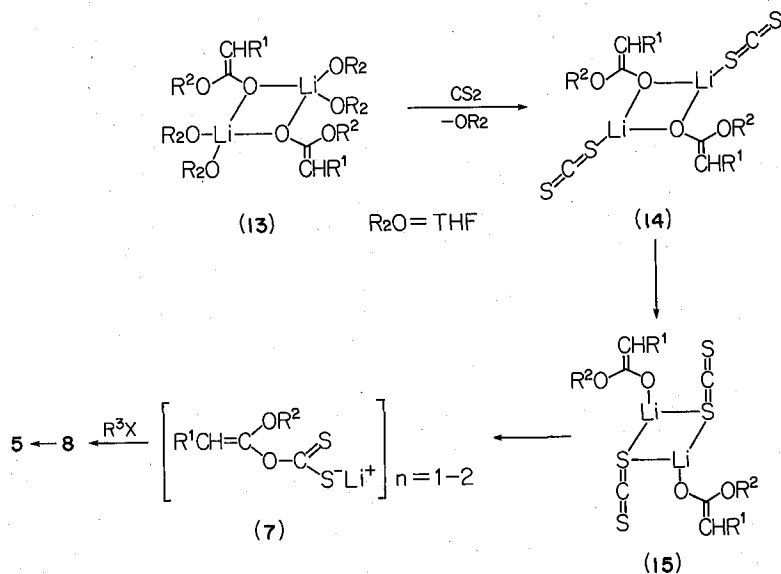
^{a)} Satisfactory microanalyses obtained: C \pm 0.32, H \pm 0.30, N \pm 0.26.

^{b)} C=O stretching band of **5** and C=C stretching band of **11**. IR spectra of **5** were measured in neat and those for **11** in nujol.

^{c)} Corresponds to the molecular ion peak in the case of **5** and [M-HN(*i*-C₃H₇)₂]⁺ ion peak in the case of **11**. The molecular ion peaks for **11** were not observed and [M-HN(*i*-C₃H₇)₂]⁺ ion peaks were those having highest mass to charge ratio.

EXPERIMENTAL

Materials and Apparatus. All the reagents and solvents were obtained commercially. Melting points were determined on a Yamato Capillary Melting Point Apparatus. The boiling points were determined by ordinary distillation. Infrared spectra were recorded on a JASCO IR-810 spectrophotometer. ¹H-NMR spectra were recorded on a Varian VXR-200 spectrometer. The mass spectral data were obtained on a LEOL JMS-DX-300 instrument. The microanalyses were determined by using a Yanaco MT-3 instrument.



Scheme 3.

General Procedure for the Preparation of α -Alkoxy carbonyl Ketene Dithioacetals (5) (Table I). A 250 ml round bottom flask was equipped with an addition funnel and a magnetic stirrer. The system was swept with dry nitrogen and a solution of diisopropylamine (3.0 g, 0.03 mol) in tetrahydrofuran (THF) (25 ml) was added. After cooling in an ice bath, a hexane solution of butyllithium (18.7 ml of 1.6 M solution) was added during 15 min and the mixture was stirred for an additional 15 min. To this solution was added carboxylic ester **1** (0.03 mol) over a 15 min period and the stirred solution was maintained at 0°C for 30–40 min. The contents were then cooled to –78°C in a dry ice-acetone bath and carbon disulfide (6.84 g, 0.09 mol) was added over a period of 30 min. The temperature of the mixture was not allowed to rise above –70°C during the addition. An immediate color change was observed and the mixture turned orange red after the addition of carbon disulfide. The contents were further stirred for 30 min. Alkyl halide (0.09 mol) was then added and the mixture stirred for 30 min at –78°C. The contents were then allowed to warm to room temperature and left stirring for the required time. The reaction mixture was worked up by adding water and extracting with ethyl acetate, washed several times with water and dried over Na_2SO_4 . The evaporation of the solvent afforded crude products which were distilled to furnish pure products.

General Procedure for the Preparation of *O*-(1-Alkoxy-2,2-dialkyl)vinyl *N,N*-Diisopropylammonium Dithiocarbonates (11) (Table II). A 250 ml round bottom flask was equipped with an addition funnel and a magnetic stirrer. The system was swept with dry nitrogen and a solution of diisopropylamine (3.0 g, 0.03 mol) in THF (25 ml) was added. After cooling in an ice bath, a solution of butyllithium (18.7 ml of 1.6 M solution) was added during 15 min and the mixture was stirred for an additional 15 min. To this solution was added carboxylic ester **9** (0.03 mol) over a period of

15 min and stirred solution was maintained at 0°C for 30–40 min. The contents were then cooled to –78°C in a dry ice-acetone bath and carbon disulfide (6.84 g, 0.09 mol) was added during 15 min period. The temperature of the mixture was not allowed to rise above –70°C during addition. An immediate color change was observed and the mixture turned orange red after the addition of carbon disulfide. The mixture was clear in some cases while a solid appeared on a few cases. Chlorotrimethylsilane (7.5 ml, 0.075 mol) was then added in one addition and the contents allowed to warm to room temperature after stirring at –78°C for 30 min. The reaction mixture was worked up by removing solid by filtration and evaporating the solvent to furnish orange red liquid. The treatment of this liquid with ether and dichloromethane resulted in the crystallization of pure products which were recrystallized from a mixture of ether and dichloromethane to furnish red crystals of *O*-(1-alkoxy-2,2-dialkyl)vinyl *N,N*-diisopropylammonium dithiocarbonates (11).

Treatment of a Mixture of 5f and 8f with Triethylamine and Ethyl Bromide. Triethylamine (2 ml) and ethyl bromide (4 ml) were added to a 1 : 1 mixture of 5f and 8f (2 g) and the contents left stirring at room temperature overnight. The reaction mixture was worked up by adding water and extracting with ethyl acetate and drying over Na₂SO₄. The evaporation of the solvent furnished pure 5f as revealed by the ¹H-NMR spectrum of the crude product. Bulb-to-bulb distillation of the crude product yielded pure 5f (1.93 g).

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